



Modified titanium foil's surface by high temperature carbon sintering method as the substrate for bipolar lead-acid battery



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HIGHLIGHTS

- The titanium foil is modified by high temperature carbon sintering method.
- The titanium foil sintered at 800 °C for 2 h has the greatest superior properties.
- The modified method is more simple and excellent.
- The battery with modified titanium foil has good electrochemical performances.
- The modified titanium foil can maintain stability during the cell cycle process.

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ABSTRACT

Titanium foil can be a type of ideal material as the substrate for bipolar lead-acid battery. However, it can't be directly used because it can be oxidized in the high voltage and strong oxidizing conditions. In this paper, we coat the titanium suboxide on the titanium foil surface by means of the high temperature carbon sintering method for the improvement of corrosion resistance of titanium metal and use it as the substrate to bipolar lead-acid battery to study its effect on the battery performances. Modified titanium foils are characterized by SEM, XRD, corrosion resistance test and electronic conductivity test. The electrochemical properties of the bipolar lead-acid battery are investigated by constant current charge/discharge method. The results demonstrate that the titanium foil carbon-sintered at 800 °C for 2 h has the most excellent chemical stability and electronic conductivity. Initial specific capacities of positive active material of bipolar lead-acid battery with modified titanium as the substrate at 0.25C, 0.5C, 1C and 2C discharge rate are 99.29 mAh g⁻¹, 88.93 mAh g⁻¹, 77.54 mAh g⁻¹, and 65.41 mAh g⁻¹. After 50 cycles, the specific capacity of positive active material at 0.5C is 81.36 mAh g⁻¹ and after 100 cycles, the specific capacity at 1C is 61.92 mAh g⁻¹.

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1. Introduction

Over the last few years, the hybrid electric vehicles (HEV) and electric vehicles (EV) have been developed very rapidly. As the most important part, the energy storage is obliged to supply exceptional power to all of the electronic devices [1,2]. Lead-acid battery has been one of the most prominent secondary batteries for over 150 years due to its simple structure, low cost and high recovery rate [3]. As power batteries, lead-acid battery is used primarily for typical "Start Stop" applications to hybrid and fully electric vehicles [4,5]. However, as power supply system for HEV or EV, the batteries need higher specific energy and power and longer cycle life. In

order to make lead-acid batteries have more market competitiveness, it is under an obligation to change its structure. At present tubular electrode, porous lead electrode and three-dimensional electrode have started to be studied [6–9].

Bipolar lead-acid battery as a type of promising electrochemical power source system has been the concern of researchers. Its electrochemical reaction mechanism is precisely the same as the traditional lead-acid battery, thus it has all the advantages of lead-acid battery. However, its structure and charging and discharging current transfer mode changes make it have superior properties. The schematic diagram of traditional lead-acid battery and bipolar lead-acid battery is presented in Fig. 1. As can be seen from Fig. 1, comparing with the traditional lead-acid battery, the current transfer direction is vertical to the plate and the current distribution is uniform due to the presence of the substrate inside the bipolar lead-acid battery. This can make it have the higher specific

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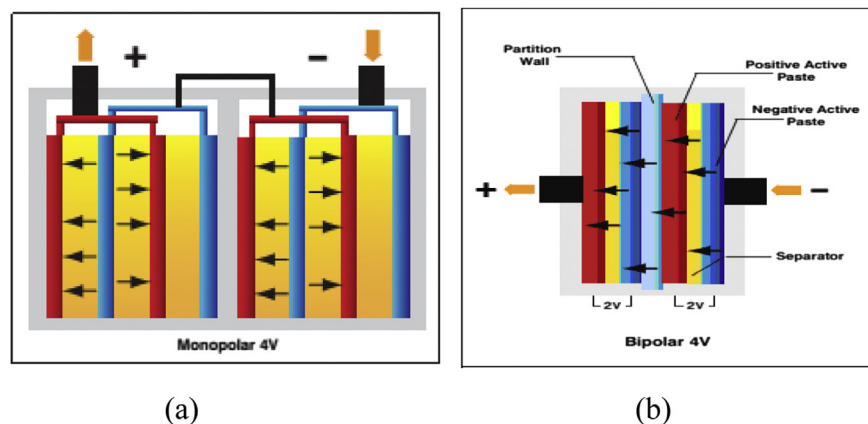


Fig. 1. The schematic diagram of traditional lead-acid battery and bipolar lead-acid battery ((a) traditional lead-acid battery, (b) bipolar lead-acid battery).[8].

energy, higher specific power [10], smaller volume, lower cost, lower ohmic loss [11], higher utilization and longer life-cycle [12]. Taking into account its these outstanding performances, the bipolar lead battery will be the development direction of lead-acid battery, especially in the fields of HEV and EV. At present, Atraverda(UK) and Effpower Company have started to develop bipolar lead-acid battery technology and the commercial bipolar lead-acid battery is also manufactured [12].

Nowadays, the research priorities of bipolar lead-acid battery are its substrate material. I. Paleska et al. [13] employed Barium metaplumbate (BMP) as a carrier and current collector in bipolar lead-acid batteries. Keith Ellis and co-workers [14,15] used Ebonex[®] Material as the substrate for bipolar lead-acid batteries. Ebonex[®] Material is the registered trade name of titanium suboxide ceramic materials. It has excellent electrical conductivity and high corrosion and oxidation resistance. It can be cheaply formulated and manufactured to form substrate plate for bipolar lead-acid batteries, and the Ebonex[®] Material is lightweight and durable high-voltage. H. Karami et al. [16] invented four types of substrate material for bipolar lead-acid battery. They were respectively lead–tin alloy substrate, carbon doped polyethylene substrate with conventional electroforming, carbon doped polyethylene substrate with chemical forming after curing and drying steps in oxidant bath and carbon doped polyethylene substrate with primary chemical oxidation in mixing step. They found that the electrochemical property of the battery was the most admirable by using the fourth kinds of material as the substrate. M. Saakes et al. [17,18] studied on the bipolar lead-acid battery as power system for hybrid vehicles. They concluded that bipolar lead-acid battery can be as the hybrid vehicle's power system due to its high energy, high power, long cycle life and low cost.

Titanium foil is also a type of ideal material as the substrate for the bipolar lead-acid battery due to its lightweight, high strength and superior corrosion resistant ability. However, pure titanium surface can be oxidized into titanium dioxide by anodic intense oxidation and high potential [19–22]. The electrochemical performances of the battery can be influenced by the poor electronic conductivity of titanium dioxide [23]. Partial reduction titanium dioxide (TiO_{2-x}) is likewise a kind of titanium oxide. Compared with titanium dioxide, it has more excellent chemical stability and electronic conductivity. This is because that losing a part of the oxygen atoms in the lattice of titanium dioxide can provide some channels for electron conduction and it has the higher chemical stability due to the change of crystal structure [24]. At present, major synthetic method of TiO_{2-x} is reducing TiO_2 at elevated

temperature and the common reducing agent is carbon(C) [25,26], hydrogen (H_2) [24] and ammonia (NH_3) [27].

In this paper, the titanium foil surface was sintered at high temperature carbon sintering method. We investigated its properties through X-ray Diffraction (XRD), scanning electron microscope (SEM), four probes and corrosion resistance tests. And then, modified titanium foils were utilized to substrate material for bipolar lead-acid battery, and the electrochemical properties of the battery are also described.

2. Experimental

2.1. Modification of titanium foil

In this paper, 0.2 mm thicknesses of titanium foils were modified by high temperature carbon sintering method. Firstly, titanium foils were covered by carbon powder in the crucible. The amount of adding carbon should need a little more in order to cover titanium foils completely and prevent titanium foils from oxidation in



Fig. 2. A 4 V experimental bipolar lead-acid battery.

Table 1

The steps of constant current charge and discharge test.

Serial number	Constant current charge cutoff voltage	Constant current charge current	Constant voltage charging time	Constant current discharge cutoff voltage	Constant current discharge current
1	4.84 V	0.25C	2 h	3.5 V	0.25C
2	4.84 V	0.25C	2 h	3.4 V	0.5C
3	4.84 V	0.25C	2 h	3.3 V	1C
4	4.84 V	0.25C	2 h	3.2 V	2C

sintering process. Secondly, titanium foils covered with carbon power were sintered at different temperature and time in the muffle furnace. At last, sintered titanium foils cooled to room temperature rapidly and cleaned the surface with distilled water to get rid of residual carbon powder.

In precious research, we found that the sintering temperature cannot exceed 800 °C. This is because when the temperature was over 800 °C, titanium foil would react with titanium oxide fiercely and it would seriously affect the titanium foil strength so that it cannot act as the substrate material for bipolar lead-acid battery. Therefore in this research, titanium foils covered with carbon power were respectively sintered at 600, 700 and 800 °C for 1 h and sintered at 800 °C for 2 h and 4 h to study on the influence of the modified titanium foils at different sintering temperature and time.

2.2. Characterization of modified titanium foil

In order to investigate the corrosion resistance of modified titanium foil, it was immersed in HF (40%): HNO₃ (60%):H₂O₂ (30%):H₂O (1:2:3:12 in volume) mixed solutions for 30 min at room temperature and then observe its surface change. Through X-ray diffraction (XRD), scanning electron microscopy (SEM) and four probe tests we characterized modified titanium foil's surface material composition, microstructure, micromorphology and electronic conductivity. In this research, XRD analysis was undertaken with a D Max-RD12Kw diffractometer with Cu K α radiation. The scan data were collected in the 2 θ range 10–90° at scan rate 2°min⁻¹. SEM was performed using a Quanta 200 instruments. The testing range of the four probe instrument is 10⁻⁶–10⁶ Ω .

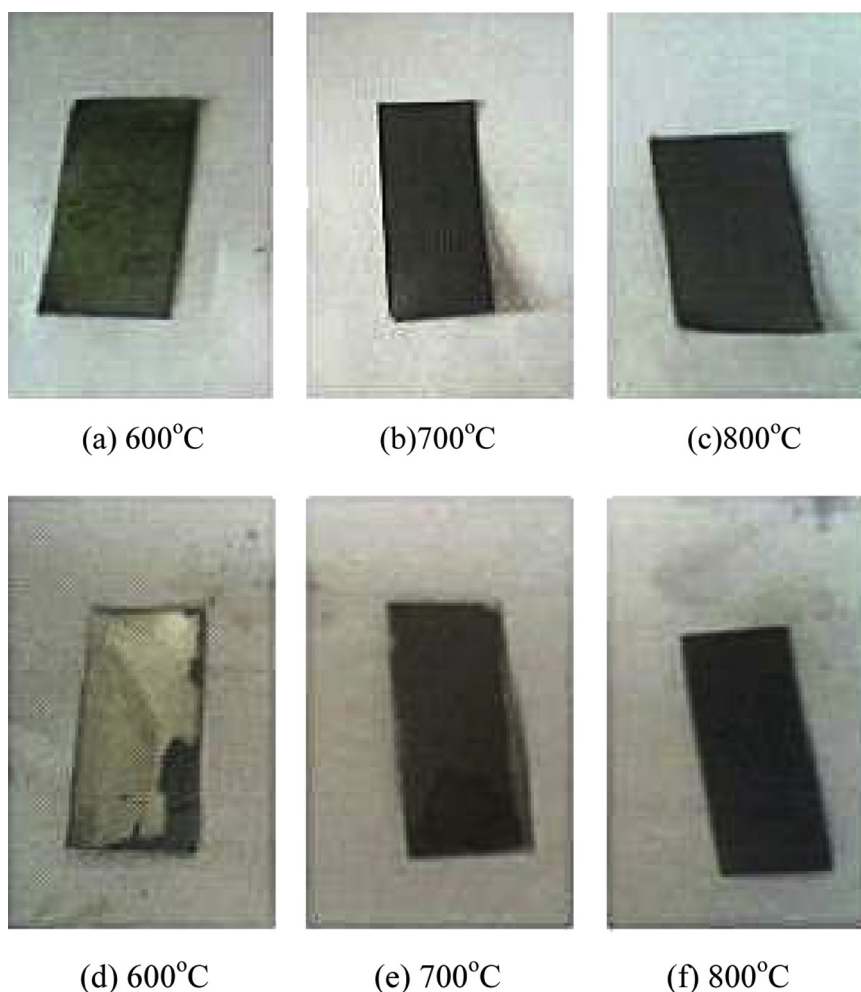


Fig. 3. The photographs of modified titanium foils sintered at different temperature before and after immersed in the corrosion liquid (a,b and c are before corrosion, d,e and f are after corrosion).

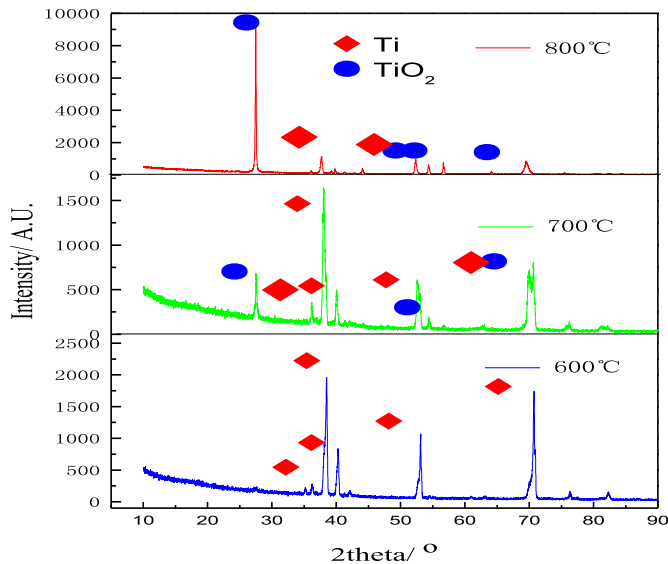


Fig. 4. X-ray diffraction patterns for modified titanium surface sintered at different temperature.

2.3. Bipolar lead-acid battery manufacture

Negative and positive pastes were prepared based on the conventional manner. Raw materials of positive paste were lead powder, red lead (Pb_3O_4), graphite, polypropylene fiber and SnSO_4 , and the raw materials of negative paste were lead powder, barium sulfate, lignosulphonate and humic acid. Firstly these raw materials were mixed in a plastic container for 10 min, and then added some distilled water to the mixture and mixed for 15 min, continued stirring and slowly added sulfuric acid (1.4 g cm^{-3}). In the process of adding sulfuric acid, the lead paste needed to hold the temperature lower than 60°C with a water cooling system. At last, lead paste required to mix for a time period so that water, sulfuric acid and lead paste can be mixed adequately.

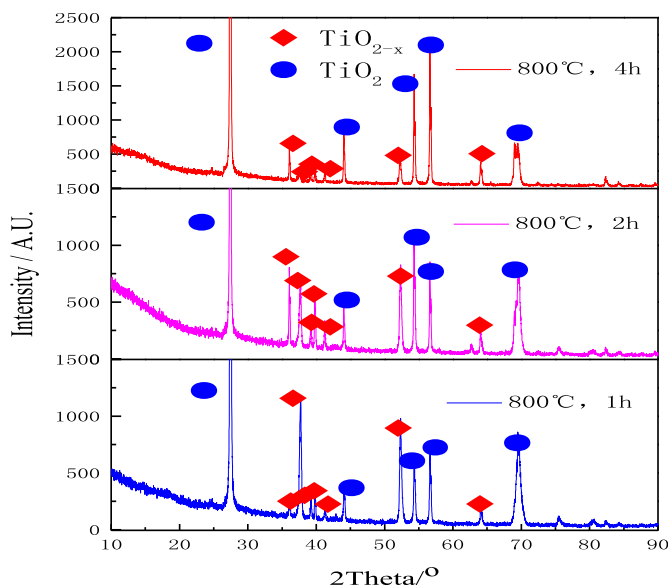


Fig. 5. X-ray diffraction patterns for modified titanium surface for different sintering time at 800°C .

After preparation of positive and negative paste, terminating anode and cathode electrodes were pasted negative and positive paste at one side of the modified titanium foils respectively. Bipolar electrodes were pasted negative and positive paste at both sides of one piece of modified titanium foil. The thicknesses of coating negative and positive paste were both 1 mm.

The pasted electrodes (including terminating and bipolar electrodes) were cured according to certain steps in constant temperature and humidity instrument. Cured plates, absorptive glass mat (AGM) as separator and 1.26 g cm^{-3} sulfuric acid as electrolyte were used in the assembling of bipolar lead-acid batteries. The number of bipolar plates determines the battery's voltage. After sealing, the experimental bipolar lead-acid batteries were assembled completely. The photograph of a 4 V experimental bipolar lead-acid battery is presented in Fig. 2.

2.4. Electrochemical tests of bipolar lead-acid battery

Before testing, batteries needed the internal formation. And then, they were tested by the constant current charge–discharge test with multi-channel battery testers (BTS-20 V 10 A, Neware, Shenzhen in China). In this research, we mainly discussed the properties of the positive active material including charge–discharge properties, rate performance and cycle life at room temperature because it is the main factor to affect the properties of the substrate material. Constant current charge and discharge steps are shown in Table 1. The current densities were calculated in accordance with Peukert equation and the specific capacities were determined on the basis of the weight of positive active material after curing.

3. Results and discussion

3.1. Characterization of the modified surface of titanium foil

3.1.1. Corrosion resistance

Digital photographs of the modified titanium foils surface at different sintering temperature before and after immersed in the corrosion liquid are shown in Fig. 3. From Fig. 3, it can be shown that before corrosion, the surface of modified titanium foil at 600°C was very inhomogeneous. When the temperature rose to 700°C and 800°C , the distribution of surface film became uniform. After corrosion the surface film of modified titanium foil at 600°C was almost completely destroyed and at 700°C was partially destroyed. However, sintered at 800°C it was hardly changed. This means that when the sintering temperature is 800°C , the film of modified titanium foil is very uniform and has the most excellent corrosion resistance.

3.1.2. Material composition and micromorphology

The X-ray diffraction patterns for modified titanium surface sintered at different temperature are presented in Fig. 4. From Fig. 4, it showed that with the increase of temperature, the content of the titanium scaled down and the TiO_2 increased gradually. At 800°C , the X-ray diffraction patterns for titanium matrix were disappeared. It means that when the temperature rises to 800°C , titanium dioxide coating on the titanium foil surface is the most uniform and dense. Compared to standard spectra of titanium dioxide (PDF#21–1276), we found that the position and intensity of the titanium dioxide diffraction peaks had some deviations. It demonstrates that the crystal structure of titanium dioxide on the titanium surface is changed and we hold the opinion that this is mainly because the carbon addition leads to lose part of the oxygen atoms of titanium dioxide resulting in the change of crystal structure.

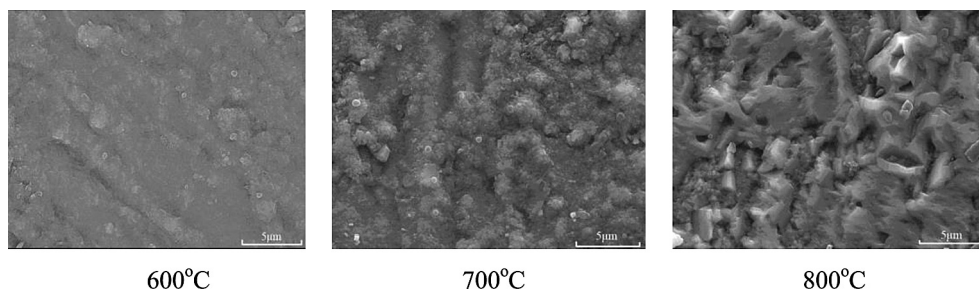


Fig. 6. SEM images of modified titanium surface under the different sintering temperature.

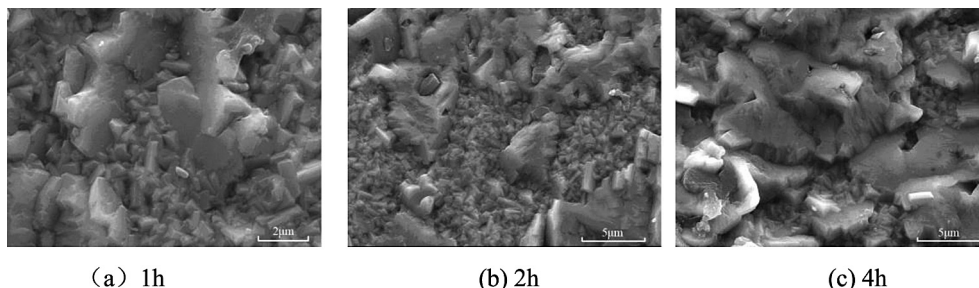


Fig. 7. SEM images of modified titanium surface for the different sintering time at 800 °C.

The X-ray diffraction patterns for modified titanium surface for different sintering time at 800 °C are shown in Fig. 5. From Fig. 5, it can be shown that there were some titanium suboxide diffraction patterns in the modified titanium surface film sintered at 800 °C. Compared to different sintering time, the content of titanium suboxide (TiO_{2-x}) in the surface film of modified titanium sintered for 1 h and 2 h was relatively more, and sintering for 4 h the content is relatively little. This indicates that too long sintering time will reduce the content of titanium suboxide in the modified titanium surface film.

Fig. 6 showed the SEM images of modified titanium surface under the altered sintering temperature. From Fig. 6, it showed that when the sintering temperature was 600 °C the surface micro-morphology was very flattening. As the temperature rose it became more and more rough. When the sintering temperature was at 800 °C, the micromorphology was very confused. It believes that crystal defects lead to the changes of crystal structure and micro-morphology of modified titanium surface and these crystal defects can provide some channel for electron conduction to improve its electronic conductivity. In this paper, we think that crystal defect is primarily due to reduction of a part of oxygen atoms in the titanium dioxide by carbon.

Fig. 7 showed the micromorphology of modified titanium surface for the different sintering time at 800 °C. From Fig. 7, it can be shown that sintering for 1 h and 2 h the micromorphology of modified titanium surface was very complex. Grain distribution was very inhomogeneous. When the sinter time is 4 h, the surface micromorphology had started to turn into tight and even. It means that the crystal mixed degree has already begun to decrease.

Table 2
The electronic conductivity of modified titanium for different sintering time at 800 °C.

Serial number	Sintering temperature (°C)	Sintering time(h)	Electronic conductivity (S cm^{-1})
1	800	1 h	0.1–0.2
2	800	2 h	0.20–0.33
3	800	4 h	0.04–0.10

3.1.3. Electronic conductivity

Table 2 showed the electronic conductivity of modified titanium foil for different sintering time at 800 °C. Compared with titanium foil sintered for different time, the modified titanium foil sintered for 2 h has the most superior electronic conductivity.

Above all, when the titanium foil was sintered at 800 for 2 h with carbon as reducing agent, it has the most marvelous chemical stability and electronic conductivity.

3.2. Electrochemical performances of bipolar lead-acid battery with modified titanium as substrate

Fig. 8 showed voltages versus initial specific capacity charge–discharge profiles for the positive active material of bipolar lead-acid battery with modified titanium foil as substrate at

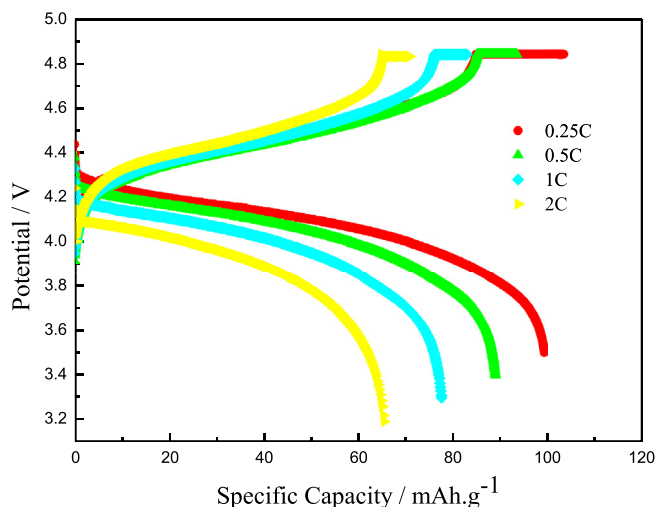


Fig. 8. The charge–discharge curves of the positive active material of bipolar lead-acid battery with modified titanium foil as substrate at different discharge rate.

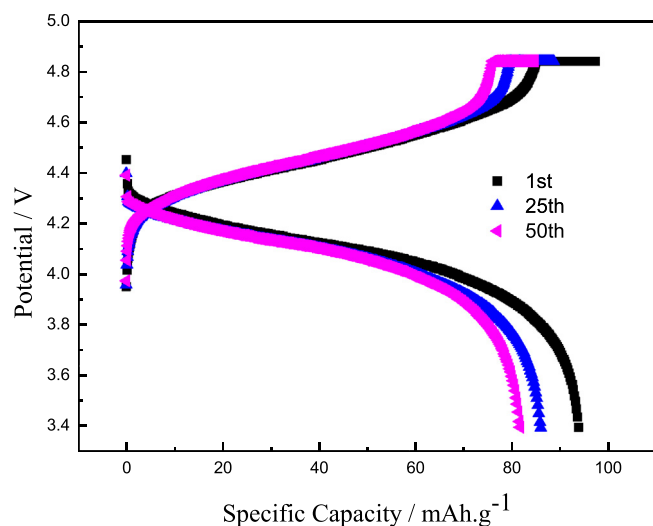


Fig. 9. The different cycle's charge–discharge curves of the positive active material of bipolar lead-acid battery with modified titanium foil as substrate at 0.5C discharge rate.

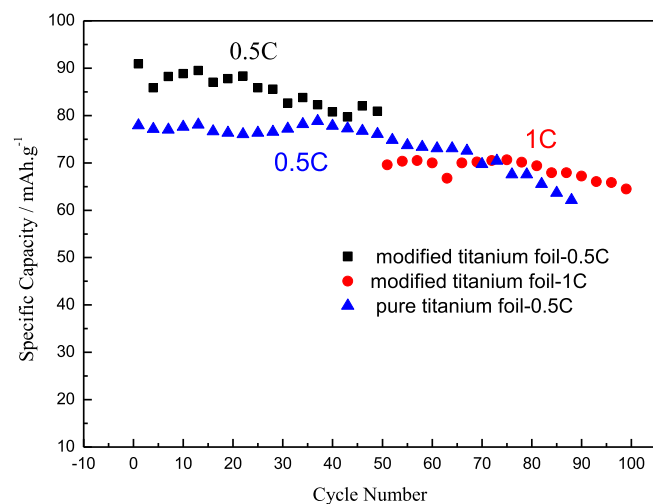


Fig. 10. The cycle life performances of the positive active material of bipolar lead-acid battery with modified titanium foil and pure titanium foil without any treatment as substrate.

different discharge rate. It was shown that the initial specific capacities at 0.25C, 0.5C, 1C and 2C discharge rate were 99.29 mAh g⁻¹, 88.93 mAh g⁻¹, 77.54 mAh g⁻¹, and 65.41 mAh g⁻¹. Compared with the discharge potential drop at different discharge rate, there were no significant changes and the specific capacity can still keep very high at high rate discharged current. It implies that the modified titanium foil as the substrate doesn't affect the charge–discharge properties of the positive active material of bipolar lead-acid battery and rate performance of the bipolar lead-acid battery with modified titanium foil as substrate is very excellent.

Fig. 9 showed 1st, 25th and 50th cycles charge–discharges curves of the positive active material of bipolar lead-acid battery with modified titanium foil as substrate at 0.5C discharge rate. From Fig. 9, it showed that the different cycle's discharge potential didn't change obviously and the specific capacity also didn't decline significantly. Fig. 10 showed the cycle life performance of the positive active material of bipolar lead-acid battery with modified titanium foil and pure titanium foil without any treatment as

substrate. With modified titanium foil as substrate, the specific capacity of positive active material at 0.5C discharge rate was 81.36 mAh g⁻¹ after 50 cycles and the specific capacity at 1C discharge rate was 61.92 mAh g⁻¹ after 100 cycles. Comparing with modified titanium foil, the specific capacity of positive active material with pure titanium foil without any treatment at 0.5C discharge rate was less and after 40 cycles started to fall significantly. These show that the cycle performance of the positive active material of bipolar lead-acid battery with modified titanium foil as substrate was very superior and the chemical stability of the modified titanium foil is also very excellent.

Above all, the bipolar lead-acid battery with modified titanium foil has the high specific capacity and good cycle performance. It means that modified titanium foil can be a kind of ideal material as the substrate for bipolar lead-acid battery.

4. Conclusions

This paper mainly studied on the properties of the modified titanium foil by high temperature carbon sintering method as the substrate for bipolar lead-acid battery. Through these studies, we can find that titanium foil sintered with carbon as reducing agency at 800 °C for 2 h has the most excellent chemical stability and electronic conductivity.

The bipolar lead-acid battery with modified titanium foil as substrate also has very superior electrochemical performance. The initial specific capacities of positive active material at 0.25C, 0.5C, 1C and 2C discharge rate were 99.29 mAh g⁻¹, 88.93 mAh g⁻¹, 77.54 mAh g⁻¹, and 65.41 mAh g⁻¹. After 50 cycles, the specific capacity of positive active material at 0.5C was 81.36 mAh g⁻¹ and after 100 cycles, the specific capacity at 1C was 61.92 mAh g⁻¹. Comparing pure titanium without any treatment they all have the obvious promotion. It shows that modified titanium foil by elevated temperature carbon sintering method can be a type of ideal material as the substrate for bipolar lead-acid battery.

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